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TECHNOLOGIC PAPERS  
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BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

NO. 77

DENSITY AND THERMAL EXPANSION OF  
AMERICAN PETROLEUM OILS

BY

H. W. BEARCE, Assistant Physicist

and

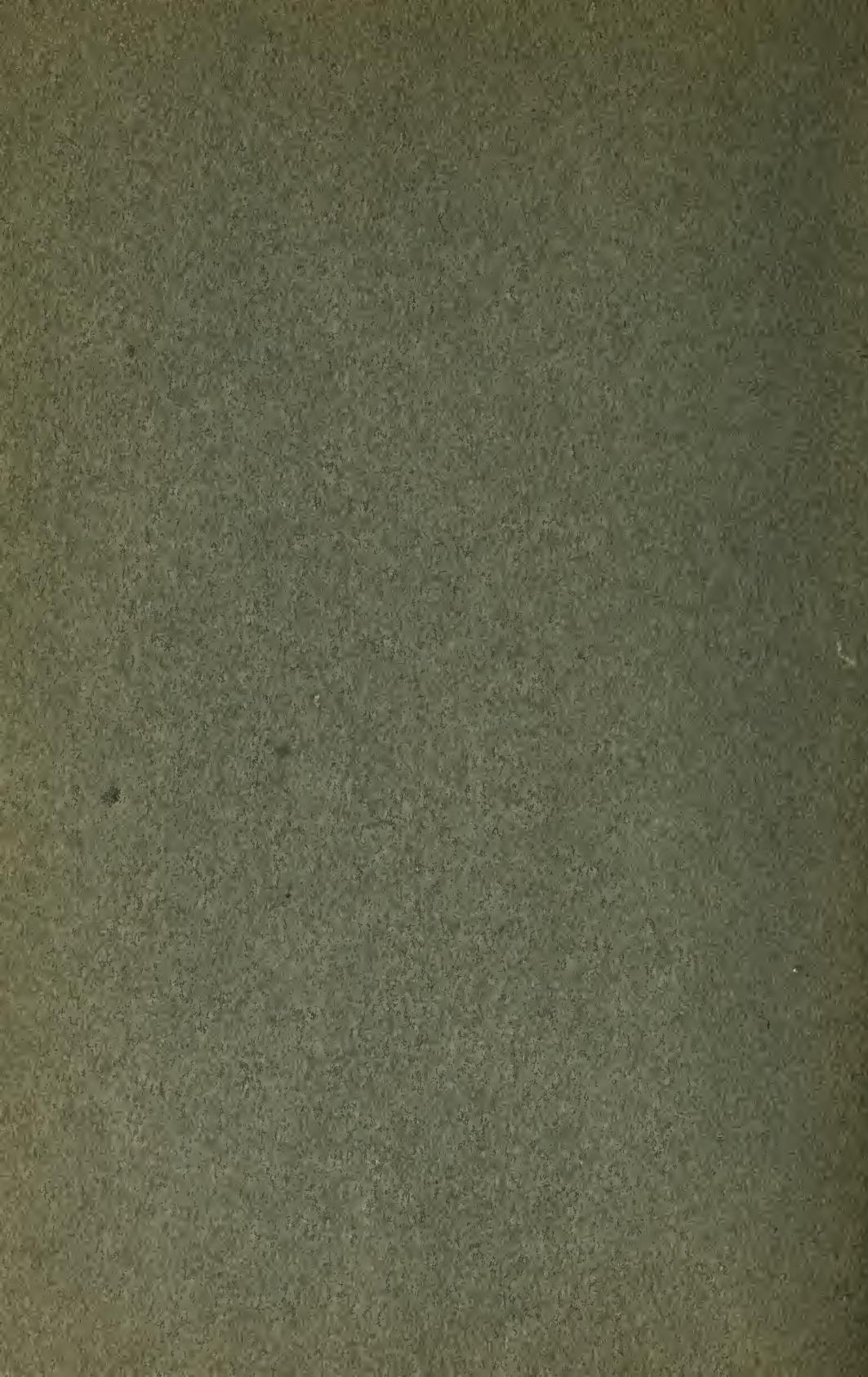
E. L. PEFFER, Laboratory Assistant

*Bureau of Standards*

ISSUED AUGUST 26, 1916



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# DENSITY AND THERMAL EXPANSION OF AMERICAN PETROLEUM OILS

By H. W. Pearce and E. L. Peffer

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## I. INTRODUCTION

### 1. OBJECT OF INVESTIGATION

The work presented in this paper was undertaken for the purpose of securing data from which to calculate standard density and volumetric tables for American petroleum oils. The data have been secured and the tables prepared and published as Circular No. 57 of this Bureau. These tables are intended to be applicable to all petroleum oils, both crude and refined, produced in the United States. They cover a density range of 0.620 to 0.950, and a temperature range of  $30^{\circ}\text{F}$  to  $120^{\circ}\text{F}$ . In addition to these, a special table for heavy lubricating and fuel oils has been prepared with a temperature range up to  $210^{\circ}\text{F}$ .

## II. MATERIAL USED

The material used in the investigation here reported was for the most part supplied by producers and refiners of oil in various parts of the United States. Oil samples were received from the States of Pennsylvania, New York, Ohio, Louisiana, Texas, Oklahoma, Kansas, Indiana, and California.

A part of the samples of lubricating oil were of unknown origin, having been submitted to the Bureau for test in connection with the fulfillment of contracts with the Government for lubricating oils.

It is assumed that the samples examined fairly represent the commercial petroleum oils produced in the United States. As the object of the investigation was to determine the rate of expansion of commercial petroleum oils, no special precautions were taken to insure more than ordinary purity in the samples collected.

## III. METHODS OF MEASUREMENT EMPLOYED

In making the density determinations on the oil samples two methods were employed: (a) The method of hydrostatic weighing; (b) the picnometer method.

In making use of the first method a sinker or plummet of known mass and volume is weighed in the sample of oil whose density is to be measured, and the density is calculated from the known volume and the difference between the weight of the sinker in *vacuo* and when immersed in the oil.

By the second method the weight of a known volume of the oil in question is determined, and the density calculated in the usual way. Details of the calculation will be given at a later point in this paper.

## IV. APPARATUS USED

The greater part of the apparatus used in this investigation has been previously described in publications<sup>1</sup> of the Bureau and need not be described in great detail here. The essential features of the apparatus used in the method of hydrostatic weighing are shown in Figs. 1 and 2. The picnometer is shown in Fig. 3.

---

<sup>1</sup> Bureau of Standards Bulletin, 9, p. 371; Technologic Paper No. 9, p. 7.

The sinker employed has a mass of 99.9630 g, and the following volumes at the temperatures indicated:

TABLE 1  
Volume of Sinker No. 7

Temperature in degrees centigrade	Volume in milliliters
0	47.6882
10	47.6998
20	47.7113
25	47.7170
30	47.7227
40	47.7339
50	47.7450

The picnometers used have the following internal volumes at the temperatures indicated:

TABLE 2

Temperature in degrees centigrade	Internal volume in milliliters	
	No. 1	No. 2
0	108.3803	109.0834
25	108.4543	109.1545
50	108.5378	109.2335
75	108.6283	109.3216
95	108.6906	109.3954

The picnometers have the following external volumes at 20° C: No. 1, 156.041 ml; No. 2, 155.592 ml. The external volume is used only in calculating the correction for air buoyancy and need not be known with great accuracy.

The temperature control bath (Fig. 1) is so arranged that either the densimeter tube *H* (Fig. 2) or the picnometer (Fig. 3) may be used. By means of an electric heating coil and a refrigerating brine coil any desired temperature between 0° and 50° C may be secured and automatically maintained within the bath.

The temperature of the bath is observed by means of mercury thermometers suspended in the bath parallel to the picnometer or densimeter tube, as shown in Fig. 1. The thermometers are subdivided to 0.1° C, and by means of a long-focus microscope are read to 0.01° C.

The thermometers used are well aged and have been frequently calibrated, and when used repeatedly over the same temperature

range in the same regular order and with occasional determinations of the ice point, the temperature observations are very consistent and are believed to be reliable to 0.01 or 0.02 C. The temperatures were nearly always read with a stationary or slowly rising meniscus, as a falling meniscus is known to be unsteady and unreliable.

## V. CALIBRATION OF APPARATUS

The density sinker and the pycnometers were calibrated by the use of pure, air-free, twice-distilled water, assuming Chappuis's<sup>2</sup> values for the density of water to be correct. Calibrations were made at each temperature at which densities were to be determined.

Throughout this paper all densities are expressed in grams per milliliter and all weights are reduced to vacuo. The densities are, therefore, in all cases numerically the same as true specific gravities at the various temperatures referred to water at 4° C as unity.

## VI. TEMPERATURE RANGE OF DENSITY DETERMINATIONS

Density determinations were made on most of the samples at the following temperatures: 0°, 10°, 20°, 25°, 30°, 40°, and 50° C. On a few samples determinations were not made at the lower temperatures, while on others the temperatures were carried up to 75°, 85°, and 95° C.

## VII. METHOD OF PROCEDURE

### 1. BY THE METHOD OF HYDROSTATIC WEIGHING

The oil sample whose density is to be measured is placed in the densimeter tube *H* with the sinker *E* immersed in it (Fig. 1) and the tube secured in position in the temperature-control bath. The temperature of the bath is then brought to the point at which the first density determination is to be made and is allowed to remain constant until the apparatus reaches a condition of temperature equilibrium. After about 20 minutes at the constant temperature observations are begun. First, a weighing is made with the sinker *E* immersed in the oil sample and suspended from the arm of a balance. The temperature is then read on each of two thermometers suspended in the tube *L*, which is immersed in the same bath and close to the densimeter tube *H*. Next, a weighing is made with the sinker *E* detached from the suspension and resting on the bottom of the tube *H*. Then, a second weighing is

<sup>2</sup> P. Chappuis, Bureau International des Poids et Mesures, *Travaux et Memoires*, XIII; 1907.

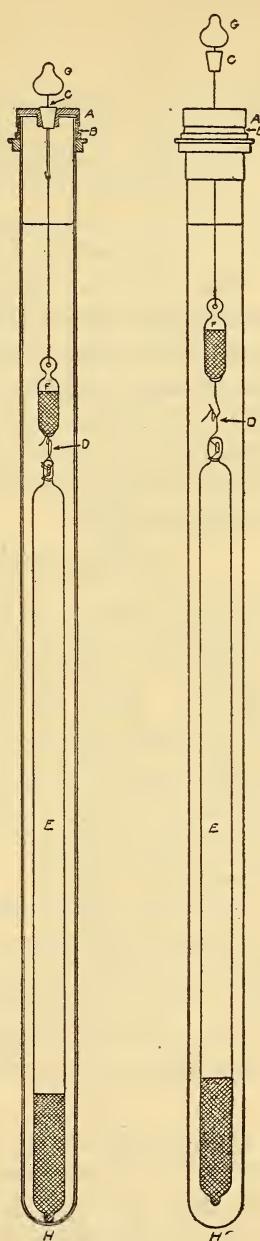
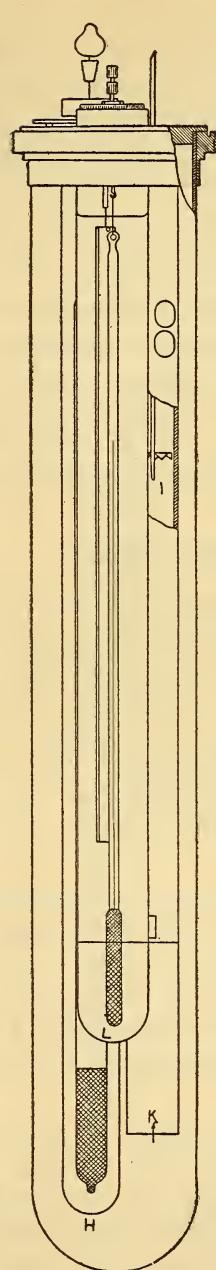


FIG. 1.—Densimeter tube, sinker and thermometers in temperature-control bath

FIG. 2.—Densimeter tube and sinker

made with the sinker *E* suspended; and, finally, the temperature is again read on the two thermometers.

By means of the small sinker *F* the suspension wire is kept in position and passing through the surface of the oil at all times, both when the large sinker *E* is suspended and when it is detached. In this way the effect of surface tension on the suspension wire is eliminated. The observations at each temperature, as outlined above, consist of two weighings with the sinker attached, one weighing with it detached, and two readings on each of two thermometers. The reason for making two weighings with the sinker attached and only one with it detached is because in the former case a slight change in the temperature of the oil makes an appreciable change in the apparent weight of the sinker on account of its large volume, while in the latter case the change is not appreciable.

After completing the observations at one point the temperature of the bath is changed to the next in the series and the process repeated in the same order.

## 2. BY THE PICNOMETER METHOD

The method of hydrostatic weighing above described is applicable only to such oils as are of sufficient fluidity to allow the sinker to readily take up a position of static equilibrium when suspended in the oil. With the more viscous oils the sensibility of the balance is greatly reduced and the weighings become more difficult to make, and of doubtful accuracy. For such oils it is therefore necessary, or at least desirable, to use some other method. The method usually resorted to is that of the picnometer or specific-gravity bottle.

For the work here described, special picnometers were designed and constructed somewhat similar to those previously used in alcoholometric determinations.<sup>3</sup> The essential features are the tube *E* (Fig. 3) extending nearly to the lower end of the picnometer, the tube *D* extending up through the bottom of the reservoir *I*, the funnel *G* and the attachment *F* provided with a stopcock.

In filling the picnometer the oil is placed in the funnel *G* and drawn in through *E* by exhausting the air through *F*. By this means much time is saved in filling the picnometer and the method is equally efficacious in emptying and cleaning the picnometer when it is desired to introduce a new sample.

When the filling is completed *F* and *G* are replaced by the caps *A* and *B*, all parts being provided with well-fitting ground joints. The picnometer having been filled, it is placed in the

temperature-control bath in place of the densimeter tube and the temperature brought to the desired point as before. The quantity of oil in the piconometer is so adjusted that when temperature equilibrium has been established the oil surface is just flush with the tip of the capillary tubes *C* and *D*. The excess oil in the reservoir *I* is removed and the interior of the reservoir

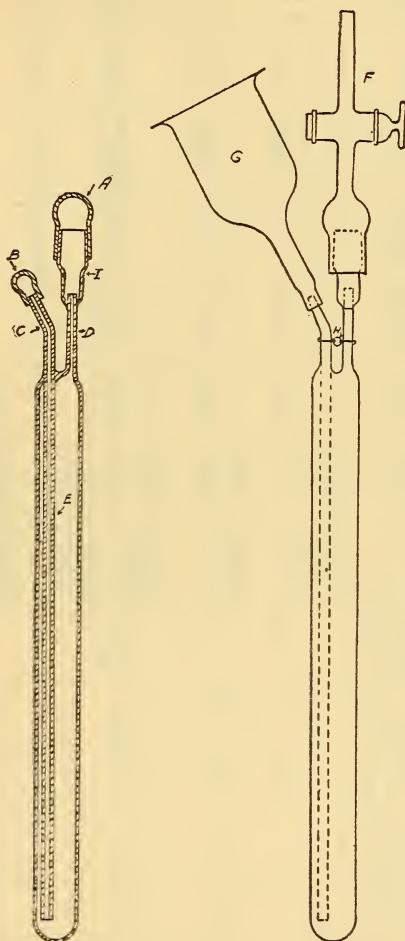


FIG. 3.—*Special piconometer*

carefully cleaned by means of a pipette, filter paper, and gasoline. The temperature is then observed and the piconometer removed from the bath, dried on the outside, allowed to come to room temperature, and then weighed.

The density of the oil at each temperature is calculated by dividing the mass by the volume; that is, by the internal volume of the piconometer at that temperature.

## VIII. SAMPLE RECORDS OF OBSERVATIONS AND CALCULATION OF DENSITY

TABLE 3

## By Method of Hydrostatic Weighing

[Sample, Texaco spirits from Oklahoma crude. Date, Mar. 16, 1914. Observer, E. L. P.]

Time	Observed temperature	Corrections to thermometers	Corrected temperature	Mean temperature t	Balance reading	Apparent weight of sinker in liquid	Buoyancy correction of sinker in liquid	True weight of sinker in liquid	Weight of displaced liquid	Volume of sinker at temperature t	Density of liquid at t/4°C	Correction to integral degrees	Density of liquid at t/4°C	Integral temperature t	
	HaaK No. 2060 24.93	Hornemann No. 9552 24.86	°C	°C	°C	g	g	g	g	ml	g/ml	°C	g/ml	°C	
10.15 a.m...			-0.01	+0.05	24.92	24.91	20.1770 83.1187 20.1773	62.9417 62.9414	-0.0089	62.9327	37.0303	47.71690	0.77604	-0.00006	0.77598
11.40 a.m...	.08	.00	-.10	-.01	24.92	24.91	21.0888 83.1508 21.0880	62.0620 62.0628							25
12.30 p.m...	10.08	10.03	-.01	+.04	24.92	24.92	20.7200 83.1379 20.7188	62.4179 62.4191	-.0087	62.0537	37.9093	47.68816	.79494	.00000	.79494
1.30 p.m...	20.01	19.95	.00	+.06	20.01	20.01	20.3571 83.1249 20.3369	62.7678 62.7680							10
2.15 p.m...	24.84	24.78	-.01	+.05	24.83	24.83	20.1808 83.1190 20.1810	62.9382 62.9380	-.0088	62.7591	37.2039	47.71130	.77977	+.00001	.77978
2.55 p.m...	29.98	29.94	.00	+.01	29.98	29.95	19.9914 83.1124 19.9914	63.1210 63.1210							20
3.40 p.m...	39.90	39.89	-.03	-.01	39.91	39.89	29.96 19.6252 83.0997 19.6254	63.1210 63.4745 63.4743	-.0089	63.1121	36.8509	47.72264	.77219	-.00002	.77217
	39.94	39.89					39.91 19.6254	63.4744	-.0089	63.4655	36.4975	47.73380	.76461	-.00008	.76453

Mass of density stinker= 95.9630 g. Buoyancy constant=1041. Air density= 0.001181 g/ml

TABLE 4  
By Pycnometer Method

[Sample, fuel oil, submitted by Atchison, Topeka & Santa Fe Railway. Date, Nov. 12, 1915. Observer, E. L. P.]

Date	Observed temperature	Corrections to thermometers	Corrected temperature	Mean temperature <sup>t</sup>	Apparent weight of pycnometer (filled)	Correction for air buoyancy	True weight of pycnometer (filled)	Weight of pycnometer (empty)	Weight of oil	Volume of pycnometer at t'	Density of oil at t'	Correction to integral degrees	Density at integral temperature
Nov. 12, 1915.	°C 25.34	°C 25.28	°C 25.02	°C 25.32	°C 25.32	°C 25.32	g 200.4333	g 200.5896	g 97.1774	ml 103.4122	g/ml 0.95350	+ .00021	g/ml 0.95371
Do.....	50.12	50.07	-.06	-.01	50.06	50.06	50.06	198.7563	198.9128	101.7354	108.5380	+ .00004	.93736
No. 17702													50
Do.....	75.67	.....	-.04	.....	75.63	75.63	197.0380	197.1966	97.1774	100.0192	108.6303	+ .00041	.92114
Nov. 13, 1915.	95.07	.....	+.01	.....	95.08	95.08	195.7308	195.8897	97.1774	98.7123	108.6908	+ .00052	.90825
													95

Buoyancy constant at 25° and 50° = 1043; air density at 25° and 50° = 0.001183.

Buoyancy constant at 75° and 95° = 1055; air density at 75° and 95° = 0.001197.

## IX. CALCULATION OF RESULTS

Having made the weighings and observed the temperatures at each of the several points at which the density is to be determined, the calculation of density is carried out by means of the following equations:

(1) By the method of hydrostatic weighing:

$$D_t = \frac{S - w \left( 1 - \frac{\rho}{8.4} \right)}{V_t} = \frac{M}{V_t}$$

$D_t$  = density of oil at the temperature  $t$

$S$  = mass of sinker

$w$  = apparent mass of sinker in oil at temperature  $t$

$\rho$  = density of air

8.4 = density of brass weights

$V_t$  = volume of sinker at temperature  $t$

$M$  = mass of oil displaced by sinker

(2) By picnometer:

$$D_t = \frac{w \left( 1 - \frac{\rho}{8.4} \right) + \rho v - P}{V_t} = \frac{M}{V_t}$$

$D_t$  = density of oil at the temperature  $t$

$w$  = apparent mass of picnometer filled with oil at temperature  $t$

$\rho$  = density of air

8.4 = density of brass weights

$v$  = external volume of picnometer

$P$  = mass of empty picnometer

$V_t$  = internal volume of picnometer at temperature  $t$

$M$  = mass of oil contained in picnometer.

## X. REDUCTION OF OBSERVATIONS

Having determined the density of the individual samples at the several temperatures, the rate of change of density with change of temperature was calculated by the application of the method of least squares to the density determinations made on each sample.

It is assumed that the expansion of any sample may be represented by an equation having the form,

$$D_t = D_T + \alpha(t - T) + \beta(t - T)^2$$

in which,

$D_t$  = density at any temperature  $t$

$D_T$  = density at the standard temperature  $T$

$\alpha$  and  $\beta$  are constant coefficients to be determined for each sample.

The various steps in the operation of working out the values of  $\alpha$ ,  $\beta$ ,  $D_T$ , and the most probable values of  $D_t$  for an average sample of oil are shown in Tables 5 and 6. From the closeness of the agreement between the observed and the calculated values of  $D_t$ , it is seen that the assumed equation can not be much in error.

A similar reduction of the observations has been made for each sample; this work, however, will not be given here in detail.

TABLE 5  
Sample of Reduction of Observations

$t$	$C_1$	$C_1^2$	$C_2$	$C_1C_2$	$C_2^2$	$D_t$	$N$	$C_1N$	$C_2N$
0	-25	625	375	-9375	140625	0.79494	+ 0.01900	-0.47500	+ 7.12500
10	-15	225	-25	+ 375	625	.78735	+ .01141	- .17115	- .28525
20	-5	25	-225	+ 1125	50625	.77978	+ .00384	- .01920	- .86400
25	0	0	-250	0	62500	.77599	+ .00005	.00000	- .01250
30	5	25	-225	-1125	50625	.77217	- .00377	- .01885	+ .84825
40	15	225	-25	-375	625	.76453	- .01141	- .17115	+ .28525
50	25	625	375	+ 9375	140625	.75683	- .01911	- .47775	- 7.16625
		7)1750		0	446250	.77594		-1.33310	- .06950
		250							

The normal equations are :

$$\Sigma C_1^2 \alpha + \Sigma C_1 C_2 \beta = \Sigma C_1 N$$

$$\Sigma C_1 C_2 \alpha + \Sigma C_2^2 \beta = \Sigma C_2 N$$

$$X_m + \frac{\Sigma C_1^2 \beta}{n} [D_t]_m$$

in which

$$C_1 = t - t_m \quad (t_m = \text{mean temperature})$$

$$C_2 = C_1^2 - [C_1^2]_m \quad ([C_1^2]_m = \text{mean } C_1^2)$$

$$N = D_t - [D_t]_m \quad ([D_t]_m = \text{mean } D_t)$$

$n$  = number of measured temperatures in series = 7

$X_m$  = density at mean temperature =  $D_{25}$

$D_t$  = density at temperature  $t$

By solving the above normal equations, the following values of  $\alpha$ ,  $\beta$ , and  $D_{25}$  are obtained:

$$\alpha = -0.000762$$

$$\beta = -0.00000016$$

$$D_{25} = 0.77598$$

These values when substituted in the general equation give the density values shown in Table 6:

$$D_t = D_{25} + \alpha(t-25) + \beta(t-25)^2$$

$$= 0.77598 - 0.000762(t-25) - 0.00000016(t-25)^2$$

TABLE 6

$t$	$t-25$	$(t-25)^2$	$\alpha(t-25)$	$\beta(t-25)^2$	$D_t$ (calculated)	$D_t$ (observed)	Difference (obs.-cal.)
0	-25	625	+0.01904	-0.00010	0.79492	0.79494	2
10	-15	225	+ .01143	- .00004	.78737	.78735	-2
20	- 5	25	+ .00381	.00000	.77979	.77978	-1
25	0	0	.00000	.00000	.77598	.77599	1
30	5	25	- .00381	.00000	.77217	.77217	0
40	15	225	- .01143	- .00004	.76451	.76453	2
50	25	625	- .01904	- .00010	.75684	.75683	-1

The above reductions are for a sample of "Texaco spirits" from Oklahoma crude.

The density determination made on the individual samples, and the calculated thermal density coefficient for each sample are shown in the following pages. The samples in each group are arranged in increasing order of their densities at 25° C.

## XI. RESULTS IN DETAIL

TABLE 7

## Refined Oils

Locality produced	Nature of oil	Density (g/ml) at—								
		0°	10°	20°	25°	30°	40°	50°	$\alpha \times 10^5$	$\beta \times 10^7$
	Pentane.....	0.6388	.....	.....	0.6131	.....	.....	.....	103	.....
	....do.....	.6410	.....	.....	.6164	.....	.....	.....	98	.....
	....do.....	.6564	.....	.....	.6321	.....	.....	.....	97	.....
	....do.....	.6562	.....	.....	.6324	.....	.....	.....	95	.....
	Naphtha.....	.7002	.6914	0.6825	.6781	0.6736	0.6647	0.6558	89	- 1
	Gasoline.....	.7193	.7107	.7020	.6975	.6933	.6845	.6757	87	- 2
	Naphtha.....	.7237	.7150	.7062	.7019	.6975	.6887	.6798	88	- 2
Texas.....	Gasoline.....	.7506	.7422	.7339	.7296	.7256	.7172	.7087	84	- 1
Pennsylvania.....	....do.....	.7515	.7433	.7351	.7310	.7270	.7188	.7105	82	- 1

TABLE 7—Continued  
Refined Oils—Continued

Locality produced	Nature of oil	Density (g/ml) at—								
		0°	10°	20°	25°	30°	40°	50°	$\alpha \times 10^5$	$\beta \times 10^7$
California.....	Gasoline (treated)	.7532	.7447	.7362	.7319	.7277	.7190	.7104	86	— 3
Do.....	Benzine (treated)	.7641	.7556	.7473	.7431	.7389	.7305	.7220	84	— 1
Indiana.....	Naphtha.....	.7657	.7575	.7493	.7453	.7411	.7328	.7244	82	— 2
California.....	Engine distillate.....	.7879	.7799	.7719	.7679	.7639	.7559	.7478	80	— 1
Oklahoma.....	Gasoline.....	.7949	.7874	.7798	.7760	.7722	.7645	.7568	76	— 2
Pennsylvania.....	Kerosene.....	.7981	.7908	.7835	.7799	.7762	.7689	.7615	73	— 1
Do.....	.....do.....	.7990	.7918	.7845	.7809	.7772	.7700	.7627	73	0
Do.....	.....do.....	.7994	.7921	.7848	.7812	.7775	.7702	.7629	73	0
Louisiana.....	Lighthouse oil.....	.8017	.7944	.7872	.7835	.7799	.7726	.7650	73	— 2
Pennsylvania.....	Kerosene.....	.8040	.7968	.7896	.7860	.7824	.7753	.7681	72	0
Do.....	.....do.....	.8054	.7982	.7910	.7874	.7838	.7766	.7694	72	0
Ohio.....	.....do.....	.8096	.8023	.7949	.7913	.7876	.7802	.7729	73	— 1
Indiana.....	Refined.....	.8128	.8054	.7979	.7942	.7905	.7830	.7756	74	— 1
Oklahoma.....	Kerosene.....	.8136	.8062	.7989	.7953	.7916	.7842	.7769	73	0
Mid-continent.....	.....do.....	.8177	.8104	.8030	.7994	.7957	.7883	.7809	74	0
California.....	.....do.....	.8249	.8175	.8101	.8064	.8027	.7953	.7878	74	0
Do.....	.....do.....	.8301	.8228	.8155	.8119	.8082	.8009	.7935	73	0
	Burning oil (high F.T.)	.8389	.....	.....	.8220	.....	.....	.8053	67	.....
Louisiana.....	Mineral Seal.....	.8390	.8322	.8254	.8221	.8187	.8119	.8052	68	0
Pennsylvania.....	Refined.....	.8573	.8507	.8440	.8407	.8374	.8308	.8243	66	+ 1
Indiana.....	.....do.....	.8614	.8546	.8478	.8444	.8410	.8343	.8275	68	+ 1
	Neutral.....	.8646	.....	.....	.8481	.....	.....	.8317	66	.....
	.....do.....	.8714	.....	.....	.8551	.....	.....	.8388	65	.....
California.....	Stove oil (treated).....	.8763	.8692	.8620	.8585	.8550	.8479	.8408	71	+ 1
Pennsylvania.....	Refined.....	.....	.8703	.8538	.8606	.8574	.8510	.8447	64	+ 3
Do.....	Dynamo oil.....	.8300	.8736	.8672	.8639	.8607	.8542	.8478	64	0
Do.....	Refined.....	.8802	.8735	.8671	.8639	.8607	.8544	.8481	64	+ 3
Louisiana.....	.....do.....	.8832	.....	.....	.8661	.....	.....	.8498	67	.....
	Neutral.....	.8834	.....	.....	.8672	.....	.....	.8512	65	.....
Pennsylvania.....	Refined.....	.8841	.8782	.8718	.8688	.8657	.8594	.8531	62	— 3
	Marine engine.....	.8938	.....	.....	.8766	.....	.....	.8609	66	.....
	Gas engine.....	.8974	.....	.....	.8810	.....	.....	.8651	65	.....
Louisiana.....	Refined.....	.9007	.....	.....	.8838	.....	.....	.8678	66	.....
	Cylinder oil.....	.9108	.....	.....	.8910	.....	.....	.8730	$\alpha$ 76	.....
	Paraffin oil.....	.9118	.....	.....	.8947	.....	.....	.8786	66	.....
Indiana.....	Refined.....	.9111	.9045	.8980	.8948	.8915	.8850	.8786	65	+ 1
	Engine oil.....	.9124	.9053	.8988	.8956	.8924	.8859	.8794	$\alpha$ 66	+ 14
	Cylinder oil.....	.9153	.....	.....	.8971	.....	.....	.8803	70	.....
	Paraffin oil.....	.9205	.....	.....	.9036	.....	.....	.8876	66	.....
	Cylinder oil.....	.9285	.....	.....	.9086	.....	.....	.8912	$\alpha$ 75	.....
Texas.....	Refined.....	.9385	.9319	.9252	.9219	.9186	.9119	.9054	66	— 1
Indiana.....	.....do.....	.9421	.....	.....	.9221	.....	.....	.9052	$\alpha$ 74	.....
Texas.....	Gas engine oil.....	.9470	.....	.....	.9306	.....	.....	.9145	65	.....
Do.....	.....do.....	.9551	.....	.....	.9389	.....	.....	.9230	64	.....

<sup>a</sup> These samples probably contained solid particles at the low temperatures.

TABLE 8

## Crude Oils

Locality produced	D <sub>0</sub> g/ml	$\alpha^1$ 0°-25°	D <sub>25</sub> g/ml	$\alpha^1$ 25°-50°	D <sub>50</sub> g/ml	
Pennsylvania.....	0.8253	.00074	0.8067	.00070	0.7892	
Louisiana.....	.8309	.00076	.8118	.00071	.7940	
Texas.....	.8425	.00074	.8241	.00072	.8061	
Pennsylvania.....	.8432	.00072	.8251	.00069	.8078	
Louisiana.....	.8526	.00065	.8363	.00065	.8200	
Ohio.....	.8548	.00076	.8459	.00068	.8288	
Mid-continent.....	.8726	.00067	.8558	.....	.....	
Oklahoma.....	.8815	.00074	.8629	.00068	.8460	
California.....	.9082	.00070	.8908	.00070	.8734	
Do.....	.9162	.00067	.8995	.00067	.8828	
Louisiana.....	.9193	.00069	.9021	.00068	.8850	
Texas.....	.9232	.00068	.9062	.00066	.8897	
California.....	.9361	.00071	.9183	.00068	.9012	
			D <sub>30</sub> g/ml	$\alpha^1$ 30°-40°	D <sub>40</sub> g/ml	
Texas.....				.9180	.00071	.9109
Do.....				.9194	.00066	.9128
Do.....				.9296	.00067	.9229
Do.....				.9396	.00068	.9328
California.....				.9564	.00066	.9498

TABLE 9

## Fuel Oils and Heavy Lubricating Oils

Nature of oil	D <sub>25</sub> g/ml	$\alpha^1$ 25°-50°	D <sub>50</sub> g/ml	$\alpha^1$ 50°-75°	D <sub>75</sub> g/ml	$\alpha^1$ 75°-95°	D <sub>95</sub> g/ml
Autocylinder.....	0.8620	.00063	0.8462	0.00064	0.8303	0.00063	0.8177
Fuel.....	.8641	.00068	.8472	.00067	.8304	.00068	<i>a</i> .8168
Autocylinder.....	.8651	.00064	.8492	.00063	.8335	.00063	.8209
Fuel.....	.8713	.00067	.8546	.00066	.8380	.00068	<i>a</i> .8144
Gas engine.....	.8809	.00063	.8652	.00062	.8496	.00062	.8373
Locomotive.....	.9003	.00068	.8833	.00062	.8678	.00062	.8555
Noncondensing cylinder.....	.9010	.00069	.8838	.00061	.8686	.00062	.8563
Locomotive.....	.9140	.00068	.8971	.00063	.8814	.00064	.8687
Marine engine.....	.9171	.00065	.9009	.00064	.8848	.00064	.8720
Gas engine.....	.9202	.00064	.9043	.00064	.8884	.00064	.8757
Do.....	.9204	.00064	.9044	.00064	.8885	.00064	.8758
Stationary engine.....	.9285	.00064	.9126	.00063	.8968	.00063	.8842
Marine engine.....	.9386	.00064	.9225	.00064	.9065	.00064	.8936
Fuel.....	.9526	.00065	.9363	.00066	.9199	.00066	<i>a</i> .9066
Do.....	.9537	.00065	.9374	.00065	.9212	.00065	.9082

*a* Calculated from the density at 85° C.  $\alpha^1$  is the change of density per degree centigrade.

XII. PLOT OF  $\alpha$  AND  $\beta$  AGAINST DENSITY AT 25° C

Following the detailed results the values of  $\alpha$  and  $\beta$  for each sample are shown graphically, these values having been plotted against the density of the sample at 25° C.

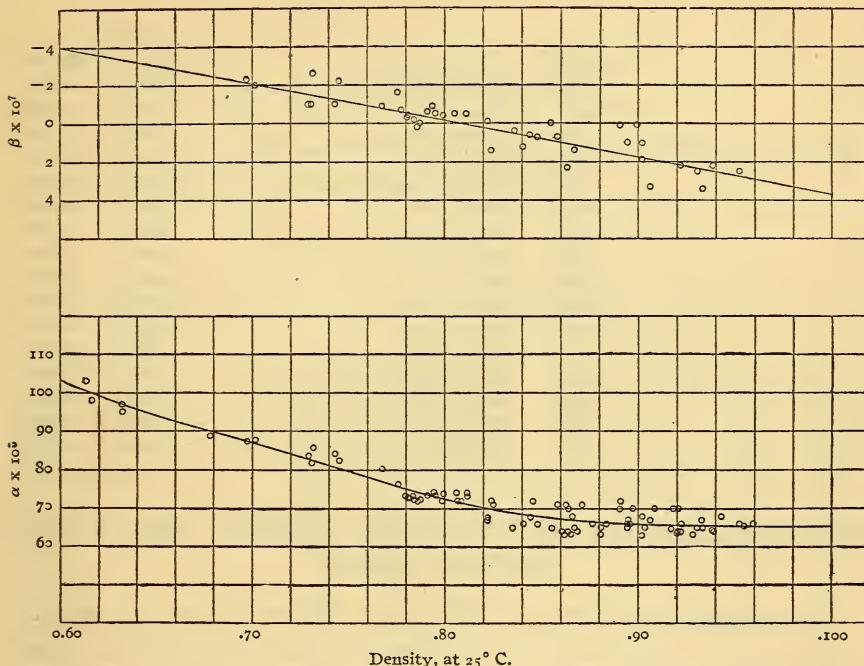


FIG. 4.—Plot of  $\alpha$  and  $\beta$  against density

A smooth curve was drawn through the points so plotted and the average values of  $\alpha$  and  $\beta$  read from this curve (Fig. 4). These values, when transformed to the basis of specific gravity at 60°/60° F were used in calculating the expansion tables published in Circular No. 57 of this Bureau.

**XIII. TABULATED VALUES OF  $D_{25}$ ,  $\alpha$ , AND  $\beta$** 

TABLE 10

Average Values of  $\alpha$  and  $\beta$  from Curves (Fig 4)

$D_{25}^{\circ}\text{C}$	$\alpha$	$\beta$	$D_{25}^{\circ}\text{C}$	$\alpha$	$\beta$
0.62.....	-0.00099	-0.0000004	0.79.....	-0.00073	0.0000000
0.63.....	.00097	.0000003	0.80.....	.00072	.0000000
0.64.....	.00095	.0000003	0.81.....	.00071	.0000000
0.65.....	.00094	.0000003	0.82.....	.00070	.0000000
0.66.....	.00092	.0000003	0.83.....	.00070	.0000000
0.67.....	.00091	.0000003	0.84.....	.00069	.0000000
0.68.....	.00090	.0000002	0.85.....	.00068	+.0000001
0.69.....	.00088	.0000002	0.86.....	.00068	.0000001
0.70.....	.00087	.0000002	0.87.....	.00068	.0000001
0.71.....	.00086	.0000002	0.88.....	.00067	.0000001
0.72.....	.00084	.0000002	0.89.....	.00067	.0000002
0.73.....	.00083	.0000001	0.90.....	.00067	.0000002
0.74.....	.00081	.0000001	0.91.....	.00066	.0000002
0.75.....	.00080	.0000001	0.92.....	.00066	.0000002
0.76.....	.00078	.0000001	0.93.....	.00066	.0000002
0.77.....	.00077	.0000001	0.94.....	.00066	.0000002
0.78.....	.00075	.0000000	0.95.....	.00066	.0000003

**XIV. CALCULATION OF STANDARD DENSITY AND VOLUMETRIC TABLES**

Measurements of petroleum oils in the United States are usually made on the basis of  $60^{\circ}\text{ F}$  as the standard temperature, and instead of density either the specific gravity at  $60^{\circ}\text{ F}$ , referred to water at  $60^{\circ}\text{ F}$  as unity, or the degrees Baumé is ordinarily employed. The volume of the oil is also usually corrected to  $60^{\circ}\text{ F}$ . For that reason it is necessary to transform the general equation representing the expansion of petroleum oils in such a way that by its use the specific gravity at any temperature can be calculated from the specific gravity at  $60^{\circ}/60^{\circ}\text{ F}$  ( $15^{\circ}56/15^{\circ}56\text{ C}$ ).

When so transformed, the equation  $D_t = D_T + \alpha_T(t - T) + \beta_T(t - T)^2$  becomes:

$$\text{Specific gravity } t/15^{\circ}56 = \text{specific gravity } 15^{\circ}56/15^{\circ}56 + \alpha_t(t - 15.56) + \beta_t(t - 15.56)^2$$

in which,

$$\alpha_t = \alpha_T + 2\beta_T(t - T), \text{ and } \beta_t = \beta_T$$

$\alpha_T$  = change of density per degree centigrade at  $25^{\circ}\text{ C}$

$\alpha_t$  = change of specific gravity per degree centigrade at  $15^{\circ}56\text{ C}$

For the purpose of calculating the volume of oil at any temperature from the volume at 60° F (15.56° C), the equation is put in the form:

$$V_t = V_{15.56\text{ C}} [1 + A (t - 15.56) + B (t - 15.56)^2]$$

in which

$$A = \frac{a_t}{D_{25}} \text{ and } B = A^2 - \frac{\beta_t}{D_{25}}$$

The volume coefficients  $A$  and  $B$  for oils of different specific gravities are shown in the following table:

TABLE 11

Specific gravity $\frac{15.56}{15.56}$ C	A	B	Specific gravity $\frac{15.56}{15.56}$ C	A	B
0.630.....	0.00156	0.0000030	0.800.....	0.00091	0.0000009
0.640.....	.00150	.0000028	0.810.....	.00089	.0000008
0.650.....	.00145	.0000026	0.820.....	.00087	.0000007
0.660.....	.00140	.0000024	0.830.....	.00084	.0000007
0.670.....	.00136	.0000023	0.840.....	.00082	.0000006
0.680.....	.00132	.0000022	0.850.....	.00081	.0000006
0.690.....	.00128	.0000020	0.860.....	.00079	.0000005
0.700.....	.00125	.0000019	0.870.....	.00077	.0000005
0.710.....	.00121	.0000018	0.880.....	.00076	.0000004
0.720.....	.00118	.0000016	0.890.....	.00075	.0000004
0.730.....	.00114	.0000015	0.900.....	.00074	.0000004
0.740.....	.00111	.0000014	0.910.....	.00073	.0000003
0.750.....	.00107	.0000013	0.920.....	.00072	.0000003
0.760.....	.00104	.0000012	0.930.....	.00071	.0000002
0.770.....	.00100	.0000011	0.940.....	.00070	.0000002
0.780.....	.00097	.0000010	0.950.....	.00069	.0000002
0.790.....	.00094	.0000009	0.960.....	.00069	.0000002

#### XV. APPLICABILITY AND ACCURACY OF THE EXPANSION TABLES OF CIRCULAR NO. 57

The expansion tables contained in Circular No. 57 are applicable to all petroleum oils, both crude and refined, produced in the United States, that are of sufficient fluidity at ordinary temperatures to allow their specific gravities to be determined by means of the hydrometer.

The accuracy with which the tables give the change of specific gravity or volume of any particular oil is dependent directly upon the closeness with which the rate of expansion of that particular oil agrees with the average rate of expansion on which the tables are based. Examination of the average curve and the closeness

with which the individual determinations agree with it indicate that it is very unlikely that the change of specific gravity per degree centigrade of any sample of oil will differ from the average change for oils of that specific gravity by more than two units of the fifth decimal place (0.00002). For example, the average change of specific gravity per degree centigrade at  $25^{\circ}$  C for oils having a specific gravity of 0.8000 is 0.00072, and it is very unlikely that any sample of American petroleum oil having a specific gravity of 0.8000 at  $\frac{25^{\circ}}{4}$  C will have a rate of change less than 0.00070 or more than 0.00074 per degree at  $25^{\circ}$  C.

Let it be supposed that the rate of expansion of some particular oil differs from the average rate by this maximum amount, then the specific-gravity value calculated from the average rate of expansion will be in error for this particular oil by 0.00002 per degree centigrade, and if the reduction is made over a temperature range of  $10^{\circ}$  C the error in the reduced specific gravity caused by the error in the assumed rate of expansion will amount to two units in the fourth decimal place.

On account of the variation in the rate of expansion of different oils of the same density it has been deemed advisable to carry the expansion tables only to the nearest five units of the fourth decimal place over a temperature range of about  $10^{\circ}$  C on each side of the standard temperature, and to the nearest unit in the third decimal place outside of this range. By thus arbitrarily limiting the implied accuracy of the tables, it is believed that the slight variations that occur between different samples of the same density need not be considered. In commercial measurements of petroleum oils density or specific-gravity determinations are seldom made with greater accuracy than one unit of the third decimal place (0.001), and it is therefore unnecessary to carry commercial oil tables beyond that point.

It is quite possible that further work on American petroleums, with greater uniformity in the methods of examination, and especially in the time of examination after the collection of the samples, may make it possible to classify the oils from different localities and to take into account the slight differences that have not been considered in the calculation of the tables of Circular 57. It may then be possible and desirable to separate the oils into groups, and for each group to construct a table that will be more exact for that group than are the general tables of Circular 57.

It may, for example, be found desirable to have different tables for Pennsylvania and for California oils, as it is generally believed that California oils have a much higher rate of expansion than do central or eastern oils. The present investigation has not shown any great difference, though the California oils have shown a slightly higher rate of expansion.

### 1. SOURCES OF ERROR

The errors entering into density determinations made by the methods described in this paper are of two kinds, namely, (a) errors in weighing; (b) errors in temperature measurement.

In the work herein reported the magnitude of these errors is, in general, such as to produce errors of not more than from two to four units in the fifth decimal place of the determined densities of the oil samples. It is very unlikely that any of the density determinations are in error by more than five units in the fifth decimal place.

The density determinations were usually made over a temperature interval of  $10^{\circ}\text{C}$ , and it is therefore apparent that the resulting error in the rate of change of density with change of temperature can not well be more than 0.00001 per degree centigrade, even if both density determinations are in error by the maximum amount and in opposite directions. Since the errors in the observed densities are, on the average, as likely to occur in one direction as in the other, and further, since the observed densities were subjected to an adjustment by the method of least squares, to determine the most probable density at each temperature, it is evident that the final errors in the densities and in the rate of change of density with change of temperature can not be very great.

It has already been pointed out that the differences occurring in the rate of expansion of two oils of the same density may be of the order of two units of the fifth decimal place per degree centigrade, and these unavoidable differences are sufficient to render insignificant the experimental errors in the density determinations.

It is evident, therefore, that expansion tables based on the results contained in this paper are susceptible of an accuracy for all petroleum oils well within the demands of observations that are themselves reliable to one unit in the third decimal place.

## XVI. RATE OF EXPANSION OF FUEL OILS AND LUBRICATING OILS OF HIGH TEMPERATURES

The Bureau has several times been requested to furnish information in regard to the rate of change of density and volume of petroleum oils at high temperatures, especially in connection with the calculation of volume of fuel oil at the standard temperature of 60° F, from its volume measured at relatively high temperatures when fresh from the topping plant. The information is also desired for use in the stillroom, where specific-gravity determinations of the different cuts must be made with as little delay as possible. It was therefore thought advisable to make density determinations on certain of the oil samples at temperatures considerably higher than 50° C, the upper temperature limit of the greater part of the investigation. Accordingly, determinations were made on several samples at temperatures up to 95° C.

From the results shown in Table 9, it will be seen that on certain samples the rate of change of density is practically the same at all temperatures between 25° and 95° C, while on other samples there is a marked falling off in the rate of expansion at the higher temperatures. This falling off is usually attributed to the melting of particles of paraffin, petrolatum, or other material that is solid at the lower temperatures and which gradually becomes liquid at the high temperatures.

The arrangement of the molecules of the liquid and the solid particles appears to be such as to prevent the same closeness of packing at the low temperatures that exists at the higher temperatures at which the solid particles have themselves become liquid. This arrangement has the effect of giving such a mixture an abnormally high rate of expansion at temperatures below the point of solidification of the particles.

In order to try the effect of dissolved paraffin on the rate of expansion of oil, density measurements were made on a sample of automobile cylinder oil not containing paraffin, and then a known amount of paraffin was dissolved in the oil and the rate of change of density again measured. The results are shown below:

TABLE 12

	Change of density per degree centigrade			
	19° to 25°	25° to 50°	50° to 75°	75° to 95°
Automobile cylinder oil.....	0.00063	0.00063	0.00063	0.00063
Same oil with 4.5 per cent paraffin added.....	.00072	.00063	.00064	.00063

It is seen that the dissolved paraffin caused a marked increase in the rate of expansion between 19° and 25° C, while at the higher temperatures the rate was not materially changed.

It is probable that if measurements had been made at lower temperatures a still further increase in the rate of expansion would have been found, but conditions were such that at that time the measurements could not conveniently be carried lower. The sample was, however, placed in a glass tube and packed in an ice bath and its appearance noted as its temperature was lowered. At temperatures above 25° C the oil was as clear as before the paraffin was added; at about 20° C it became somewhat cloudy; and at 15° C it was very cloudy or opaque, with a characteristic flaky appearance. At still lower temperatures it became practically a solid vaseline-like mass with very pronounced irregular fractures and transverse fissures.

The behavior of the above sample was very similar to that of certain other samples previously examined, in which abnormally high rates of expansion were found at the lower temperatures, and this would seem to indicate that their high rate of expansion was also due to the presence of dissolved substances that became solid at low temperature.

## XVII. COMPARISON OF RESULTS WITH PREVIOUS WORK

The results presented in this paper, so far as comparison can be made, are in substantial agreement with those given by D. Holde in his book entitled "Examination of hydrocarbon oils," and that of other experimenters; for example, Hans Höfer and Augustus H. Gill.

Since the direct object of this investigation was to obtain data from which to calculate expansion tables for petroleum oils, the work itself can perhaps best be judged by a consideration of these tables. A comparison of the tables (Circular No 57, this Bureau) with those published by the Kaiserlichen Normal Eichungs Kommission (Germany) in 1892 and republished in 1906 shows that when reduced to the same basis they are in excellent agreement throughout their entire range. Only in rare instances do the reduced specific gravities differ by more than one unit in the third decimal place. In most cases the two tables are in perfect agreement or differ by not more than five units in the fourth decimal place.

Another table that is used to some extent in this country is the Baumé table published by C. J. Tagliabue in his Manual for Inspectors of Coal Oil. It is interesting to compare this with the new table prepared by this Bureau. (Table 2, Circular No. 57.) Such a comparison shows that for the heavier grades of oil the agreement between the two tables is all that could be wished. For example, with oils having observed values of  $20^{\circ}$ ,  $30^{\circ}$ , and  $40^{\circ}$  Baumé at various temperatures, the two tables give the following values for the degrees Baumé at  $60^{\circ}$  F.:

TABLE 13

[A=Data in this column from Bureau of Standards Circular No. 57, Table 2. B=Data in this column from Tagliabue's Manual for Inspectors of Coal Oil, 8th ed.]

Observed temperature, °F	Observed values, $20^{\circ}$ Bé.		Observed values, $30^{\circ}$ Bé.		Observed values, $40^{\circ}$ Bé.	
	Degrees Baumé at $60^{\circ}$ F		Degrees Baumé at $60^{\circ}$ F		Degrees Baumé at $60^{\circ}$ F	
	A	B	A	B	A	B
30.....	21.7	21.8	32.0	32.2	42.4	42.5
40.....	21.2	21.1	31.4	31.4	41.6	41.6
50.....	20.6	20.5	30.7	30.7	40.8	40.8
60.....	20.0	20.0	30.0	30.0	40.0	40.0
70.....	19.4	19.4	29.3	29.3	39.2	39.2
80.....	18.9	18.9	28.7	28.6	38.5	38.4
90.....	18.3	18.4	28.0	28.0	37.7	37.6
100.....	17.8	17.8	27.4	27.3	37.0	36.8
110.....	17.2	<sup>a</sup> 17.3	26.8	<sup>a</sup> 26.7	36.3	<sup>a</sup> 36.1

<sup>a</sup> Extrapolated from  $109^{\circ}$  F.

For the lighter oils, however, the agreement between the two tables is by no means as good as for the heavier oils. A comparison of  $70^{\circ}$ ,  $80^{\circ}$ , and  $90^{\circ}$  Baumé is given in Table 14.

TABLE 14

[A=Data in this column from Bureau of Standards Circular No. 57, Table 2. B=Data in this column from Tagliabue's Manual for Inspectors of Coal Oil, 8th ed.]

Observed temperature, °F	Observed values, 70° Bé.		Observed values, 80° Bé.		Observed values, 90° Bé.	
	Degrees Baumé at 60° F		Degrees Baumé at 60° F		Degrees Baumé at 60° F	
	A	B	A	B	A	B
30.....	74.3	74.3	85.0	84.6	95.7	94.7
40.....	72.8	72.7	83.2	83.0	93.8	93.2
50.....	71.4	71.3	81.6	81.5	91.9	91.7
60.....	70.0	70.0	80.0	80.0	90.0	90.0
70.....	68.6	68.7	78.4	78.5	88.3	88.4
80.....	67.4	67.5	76.9	77.1	86.5	87.0
90.....	66.1	66.3	75.5	75.7	84.8	85.6
100.....	64.9	65.1	74.0	74.4	83.1	84.2
110.....	63.6	<sup>a</sup> 64.0	72.5	<sup>a</sup> 73.2	81.5	<sup>a</sup> 82.8

<sup>a</sup> Extrapolated from 109° F.

It will be seen from the above that some of the values of the degrees Baumé at 60° F, as given in Tagliabue's manual, fail to agree with those based on this investigation by more than 1° Bé. It should also be noted that the Baumé hydrometers made by Tagliabue for petroleum oils are not based on the modulus 140 adopted by other manufacturers and in general use in the United States, and as a result they read too high by varying amounts up to about 0.9° Bé. for a 90° Bé. oil. That being the case, if a Tagliabue Baumé hydrometer is used in a light petroleum oil at a high temperature, and Tagliabue's table is used for reducing the observed value to the standard temperature of 60° F, the final result may be in error by more than 2° Bé., as compared with a correct American standard Baumé hydrometer used in connection with the oil tables of this Bureau. (Circular No. 57.)

### XVIII. CONCLUSION

In conclusion, the authors would state that while the results of the investigation here reported are considered adequate as the basis of petroleum-oil tables for ordinary commercial use, it is very desirable that the work be continued in order that the small differences in the rate of expansion of oils of the same density, but from different oil fields, may be further studied. It is very probable that further investigation would render possible the

calculation of expansion tables that would be somewhat more accurate for the oils of any given locality than are the general tables based on the average results herein reported.

Other considerations than the need for reliable expansion tables also make it important that our knowledge of the physical properties of oils be further extended, and for that purpose a comprehensive and thorough investigation should be carried out. It is believed that samples of crude petroleum should be obtained from all the important oil fields of the world and the processes of refining carried out in the laboratory on a sufficiently large scale to closely approximate conditions and results of the commercial refineries.

Lubricating oils especially are in great need of further study in order that the interrelation of their measurable characteristics may be determined. Only by a systematic study of the properties of oils and their relation to each other will it become possible to make "specifications" for lubricating oils that will be susceptible of interpretation or enforcement, or to discover the fundamental nature of the material.

WASHINGTON, March 11, 1916.









